ASTM D2887 Simulated Distillation Calibration Mixture Analysis Using a Differential Acceleration Column

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Introduction

Differential acceleration (DA) columns offer improved separation performance by employing a retention gradient in the column as a function of length. Retention gradients can be created in several ways. This application note focuses on variable stationary phase thickness (VSPT), which offers the most compatibility with conventional GC hardware. In fact, our VSPT columns are fully compatible with your existing methods with no modifications to your GCs.

Our patented* DA columns typically achieve 20-40% faster separations with 15-30% better chromatographic resolution, as compared to existing columns. Further, DA columns with VSPT often offer larger sample capacity and less retention shifts due to overloading.

Historically, faster separations come at a significant cost due to additional hardware modules (low-thermal-mass ovens, etc) or method compromises (high-split injection, cryo-focusing). DA columns offer faster separations without hardware changes and minimal method changes (usually a different flow rate or temperature program).

In this note, we look at Simulated Distillation (ASTM D2887) with the C_6-C_{44} boiling point range calibration mixture. Low-split and on-column injections were performed with a megabore DA-1 column. Run times ranging from 8.4 - 8.6 minutes were achieved with ease, which is significantly faster than most "fast" methods currently in use (we have not seen faster than 14 minutes). Alkane resolution and peak shape is good (considering the extremely large range of mass-on-column required for this analysis).

* **Patents: US 8323504, US 8377309, US 8329038**
Patent Pending: US 20120118156

Methodology

A standard Agilent 7890 GC platform with a split/splitless inlet, 7683b autosampler, and a flame ionization detector was used for GC analysis. Additional experimental details for the GC conditions are provided after each chromatogram below.

The column dimensions were 10 m x 0.53 mm (ID) with a DA-1 dimethyl polysiloxane phase coating with a linear thickness gradient starting at 0.700 μm at the head of the column and 0 μm at the end of the column.

The D2887 calibration mixture was acquired from Spectrum Quality Standards (#2887-1) and contains an assortment of straight-chain alkanes from *n*-hexane (C_6H_{14}) to *n*-tetratetracontane ($C_{44}H_{66}$), which is shown in detail in *Table 1*. The mixture was diluted (1:100 m/m) with carbon disulfide (CS_2), taking care to heat the standard ampule to ensure quantitative transfer of the heavier alkanes into the dilution vessel.

Results

Figure 1 shows the D2887 calibration mixture separation using split injection (2 μL at 20:1). C_{44} elutes at 8.4 minutes and exhibits well-defined and separated peaks. The alkanes are separated with excellent resolution and minimal tailing. Reduction of the split ratio (down to 2:1) and increasing the sample volume (up to 5 μL) did not cause any significant column overloading or retention shifting.

Figure 2 shows the D2887 calibration mixture separation using on-column injection (0.5 μL). The oven conditions were altered slightly from *Figure 1* to achieve better on-column focusing and to better retain the lighter alkanes, relative to the solvent. A custom inlet liner, manufactured in-house, was used to interface a standard 10 μL syringe to the head of the column. A conventional autosampler (Agilent 7683b) was used with regular “fast” settings. Slow plunger options were tested, but did not offer any significant improvements in the separation. Under these conditions, the separation takes about 15 seconds longer (C_{44} elutes at 8.6 minutes). The analysis still offers great resolution for most Simulated Distillation applications in 40% less time than the fastest on-column D2887 methods we have found.

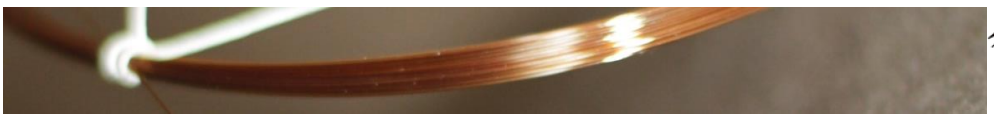
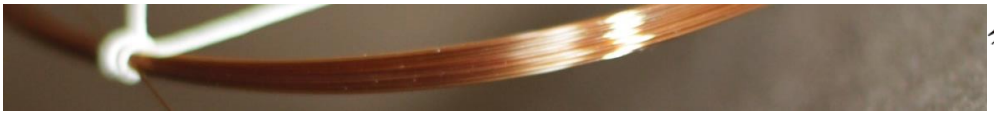


Table 1. D2887 Test mixture details and peak labels. The mass concentrations reflect the original standard tolerances. The standard was diluted (1:100 by mass) in CS_2.

Peak #	Name	Formula	CAS #	% Mass
6	n-Hexane	C6H14	110-54-3	4.92-5.94
7	n-Heptane	C7H16	142-82-5	4.93-6.00
8	n-Octane	C8H18	111-65-9	7.88-7.97
9	n-Nonane	C9H20	111-84-2	7.89-7.93
10	n-Decane	C10H22	124-18-5	11.83-11.90
11	n-Undecane	C11H24	1120-21-4	11.83-12.28
12	n-Dodecane	C12H26	112-40-3	11.77-11.89
14	n-Tetradecane	C14H30	629-59-4	11.79-11.90
16	n-Hexadecane	C16H34	544-76-3	7.93-9.91
18	n-Octadecane	C18H38	593-45-3	3.93-4.96
20	n-Eicosane	C20H42	112-95-8	0.992-1.98
24	n-Tetracosane	C24H50	646-31-1	0.987-1.99
28	n-Octacosane	C28H58	630-02-4	3.93-4.96
32	n-Dotriacontane	C32H66	544-85-4	0.986-1.01
36	n-Hexatricontane	C36H74	630-06-8	0.985-1.02
40	n-Tetracontane	C40H82	4181-95-7	0.983-1.09
44	n-Tetratetracontane	C44H90	7098-22-8	0.787-1.01



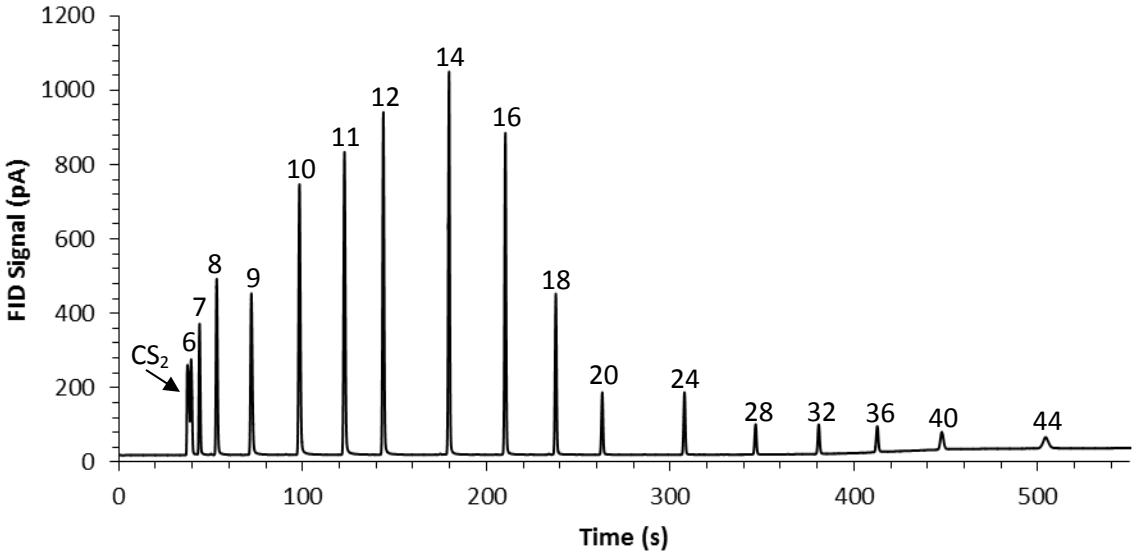
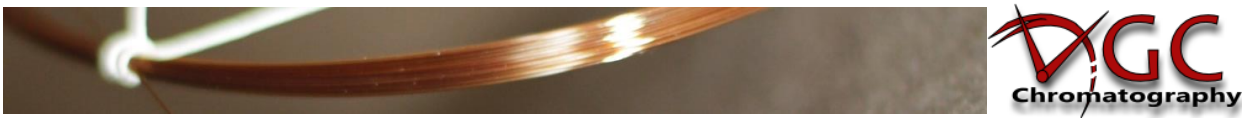


Figure 1. Chromatogram of the diluted D2887 calibration mixture (100:1 m/m in CS_2) using a standard split/splitless injection. The n-alkane peaks are labeled by carbon number.

Table 2. GC Experimental Conditions (Split Injection)

Autosampler Syringe Size (µL)	10
Injection Volume (µL)	2
Carrier Gas Used	Hydrogen
Column Flow Rate (mL/min)	4
Split Ratio	20:1
Inlet	320° C (Straight 2 mm liner with Deact. Wool)
Oven Temperature Program	1 min hold at 70° C, then 45°C/min to 330° C with 3 min hold
FID Temperature	350° C
Make-up Gas	Hydrogen
Make-up Flow Setting	Constant make-up flow
Make-up Flow + Column flow (mL/min)	0.1
Hydrogen Flow (mL/min)	40
Air Flow (mL/min)	450
FID Data Collection Rate (Hz)	100
Data Processing Software	ChromaTOF version 4.50.8



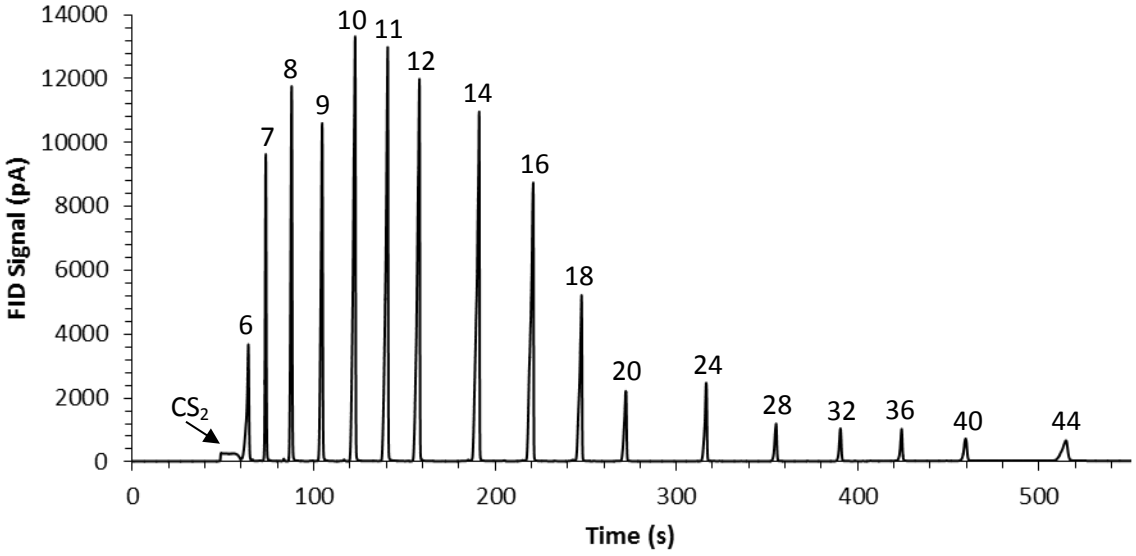


Figure 2. Chromatogram of the diluted D2887 calibration mixture (100:1 m/m in CS_2) using on-column injection (0.5 µL at 275° C). The n-alkane peaks are labeled by carbon number.

Table 3. GC Experimental Conditions (On-Column Injection)

Autosampler Syringe Size (µL)	10
Injection Volume (µL)	0.5
Carrier Gas Used	Hydrogen
Column Flow Rate (mL/min)	4
Split Ratio	20:1
Inlet	275° C (custom on-column inj. Liner)
Oven Temperature Program	0.5 min hold at 40° C, then 45°C/min to 330° C with 3 min hold
FID Temperature	350° C
Make-up Gas	Hydrogen
Make-up Flow Setting	Constant make-up flow
Make-up Flow + Column flow (mL/min)	0.1
Hydrogen Flow (mL/min)	40
Air Flow (mL/min)	450
FID Data Collection Rate (Hz)	100
Data Processing Software	ChromaTOF version 4.50.8

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